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Pore Geometry and Nonoutflow of the Nonwetting Liquid Dispersed in Nanoporous Medium

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Abstract

The phenomenon of transition to a metastable state of the liquid dispersed in confinement was investigated in this work. Two hydrophobic porous media with similar characteristics has been used. This porous media had identical material (SiO_2), surface modification and comparable pore size distribution function, but different pores geometry: quasi-cylindrical (SBA) and quasi-spherical (KB). The characteristics of porous media and results of investigation the non-wetting liquid dispersion in porous media phenomenon at temperatures system from 293 to 343 K and filling the pores of porous media from 10 to 100 percents was presented.

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Keywords: Porous media; non-wetting liquid; entrapment of liquid;

1. Introduction

Now time the interest to the phenomena related with interaction non-wetting and wetting liquids with porous media is highly increased. The threshold effect of dispersion non-wetting liquid in porous media [1] is one of these

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phenomena. It was shown [1] that the observed transition to a metastable state of the liquid dispersed in confinement takes place in a narrow range of degrees of pores filling and temperatures. In work [2] was suggested qualitative interpretation of this phenomenon. The effect of dispersion, according to [2], has been explained by the appearance of a potential barrier due to fluctuations of the collective "multiparticle interaction" of liquid nanoclusters in neighboring pores of different sizes on the shell of the fractal percolation cluster of filled pores. Further investigation shown, that the effect dispersion depends on the pore size distribution function and temperature [3].

In this work was investigated phenomenon of nonwetting liquids nonoutflow from hydrophobized porous media. The samples under investigation had similar pore size distribution functions and modified surfaces, but their pore geometry was different. The influence of pore geometry, temperature and degree of filling of pores on this phenomenon was defined.

2. Materials and Methods

The research was carried out for two types of the porous media: a quasi-cylindrical pores (SBA) and the quasi-spherical pores (KB). Initial sample SBA was created in Moscow State University by method [4]. The sample KB was a commercially manufactured «Silica gel» (#717185) produced by Sigma-Aldrich. The samples surface modification was carried out by method [5]. After modification the following characteristics of this samples was determined: density (ρ), specific pore volume (V_{por}), specific surface area (S_{por}) by BET [6] and pore size distribution (PSD) function f(r) by BJH [6]. The measurements was carried out using a helium pycnometer ULTRAPYC 1200e and automatic gas sorption analyzer Autosorb IQ the both manufactured by Quantachrome Instruments (USA). The results presented in Table 1 and Fig. 1(a).

Table1. Characteristics of the samples.

Sample	S_{por}, m^2/g	V_{por}, cm^3/g	ρ, g/cm^3
KB-1- C1	340	0,47	1,82
SBA-1-C1	490	0,81	1,81

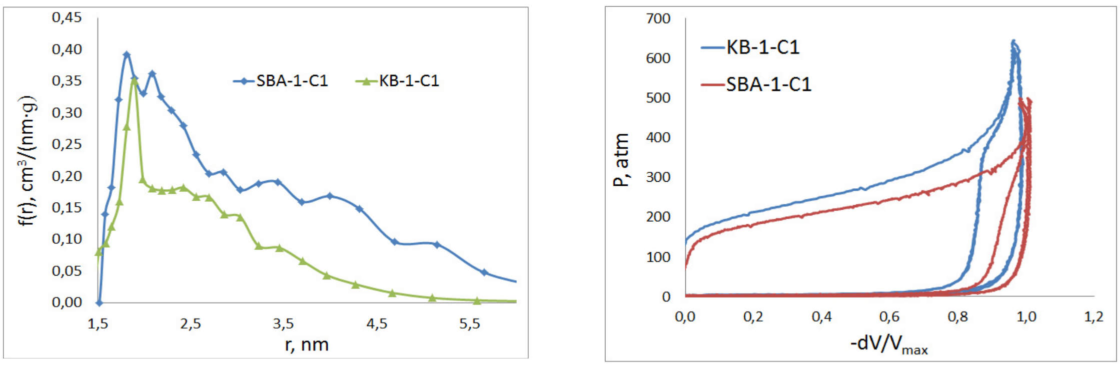

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Fig. 1. (a) PSD of porous media KB-1-C1 and SBA-1-C1; (b) dependences of the volume change on pressure for the system water- KB-1-C1 and system water -SBA-1-C1.

The surface modification of samples was tested by method [7] at temperature 293 K. The experimental dependences of the volume change on pressure for the systems water – KB-1-C1 and water – SBA-1-C1 presented on Fig. 1 (b). The compressibility of the measuring cell, liquid and porous media skeleton has been taken into account and dependences normalized by pore volume. This dependences confirms that this porous media has similar modification, PSD and hydrophobic.

The phenomenon of transition to a metastable state of the liquid dispersed in confinement was investigated according to [1]. The porous media was placed in a high-pressure cell. The free volume of the high-pressure cell was filled with liquid. After the rod installed in the cell, system assembly was placed on the movable platform of the measuring stand. The system was kept at a constant temperature for more than one hour. The movement of the rod in the high-pressure cell leads to volume reduction inside the cell and pressure increase in the system, due to deformation of the system and filling the porous medium by liquid. Then the rod was moved out from the cell the pressure in cell reduced, elastic deformations removed and part of the liquid follows out from the porous media. At least two cycles in one experiment was carried out. The fraction of the filled volume of the porous media in first cycle was from 10 to 100 percents. Calculation was carried out according to [1]. The fraction of the filled volume of the porous media (θ_{in}) was defined as ratio of the filled volume of the porous media at the total pore volume of a porous media. Fraction of the porous media volume filled with liquid after excess pressure decrease to «zero» (θ_{out}) calculated as ratio the volume of porous media filled with liquid after excess pressure decrease to «zero» at the total pore volume of a porous media.

3. Results

Dependences of $\theta_{out}(\theta_{in})$ at different temperatures 293 K, 303 K, 313 K, 323 K, 333K, 343 K for both systems water - KB-1-C1 and water - SBA-1-C1 was obtained. The results presented on Fig. 2. For this system $\theta_{out} \approx \theta_{in}$ up to $\theta_{in} \sim 90\%$ and not depends on the temperature. For $\theta_{in} > 90\%$ temperature increase leads to θ_{out} decrease and this effect greater for KB-1-C1 than for SBA-1-C1.

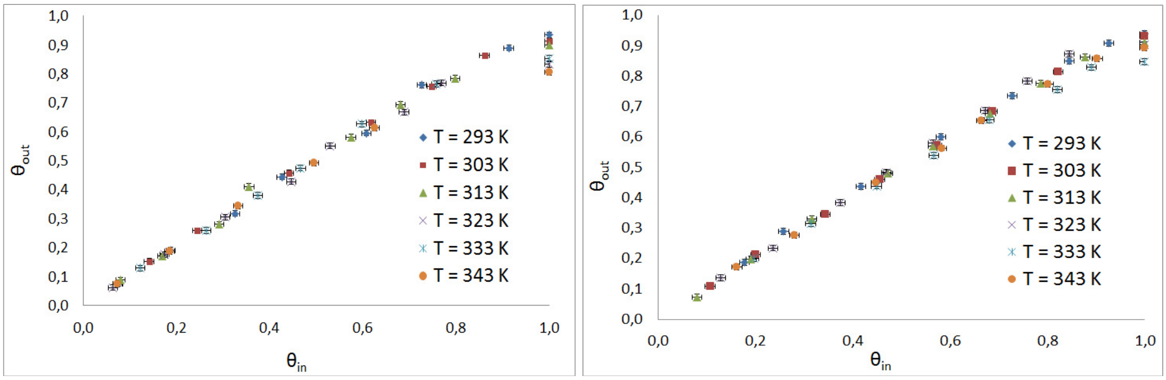

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Fig. 2. Dependences of $\theta_{out}(\theta_{in})$ at different temperatures for: (a) KB-1-C1 – water system; (b) SBA-1-C1 – water system.

This effect is due to liquid outflow from the small pores (see Fig. 1(a)) because of intrusion pressure in second cycle (see Fig. 1(b)) higher than in first cycle and the probability of liquid outflow increases with increasing temperature, according to [1, 3].

4. Discussion

The data obtained in this work is similar to the results that was obtained for the system Fluka 100 C8 – water and for the system Fluka 100 C18 - water at the same temperatures [3]. The dependences $\theta_{out}(\theta_{in})$ for the system KB-1-C1 – water at different temperatures can be explained according to the model described in [3]. According to [3], the outflow must be in the first place is energetically favorable process, and secondly the paths for liquid outflow from the granules of a porous media need to exist. The second condition is fulfilled for this system because the volume of porous media filled with liquid is exceeds 80 %. The intrusion and extrusion pressures for PSD of KB-1-C1 was calculated according to [3, 7]. As results, the intrusion pressure is in range of measurement error equal to the pressure that was observed in the experiment. The pressure at which the liquid flows out from the pores of a porous media for the small pores (< 2 nm) is close to be zero and for another is negative. Thus, for the KB-1-C1 – water system the liquid outflow for the most of pores is energetically unfavorable.

The intrusion and extrusion pressures for PSD of SBA-1-C1 was calculated. The intrusion pressure is in range of measurement error equal to the pressure that was observed in the experiment. The extrusion pressure should be greater than 50 atmospheres. So, for the system SBA-1-C1 – water the outflow of the liquid is energetically favorable. But in the experiment we observe that the liquid does not flow out of the pores of a porous media SBA-1-C1. This can be explained as breaking paths for liquid outflow from the pores by emptying of the pores on the shell of granule, according to [8]. The porous media SBA-1-C1 is a quasi-cylindrical parallel channels. In such system the each pore has "neighbors" ~ 2. Breaking paths for liquid outflow from the pores leads to the blocking the liquid in another pores.

According to experimental data, phenomenon of the liquid nonoutflow is mostly dependent on quantity of neighbors than on the pore geometry.

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References

[1] Borman VD, Belogorlov AA, Byrkin VA, Tronin VN, Troyan VI. Observation of a dispersion transition and the stability of a liquid in a nanoporous medium. *JETP Lett* 2012; 95: 579-582.
[2] Borman VD, Belogorlov AA, Byrkin VA, Tronin VN. et al. Kinetics of the dispersion transition and nonergodicity of a system consisting of a disordered porous medium and a nonwetting liquid. *Phys. Rev. E* 2013; 88:052116.
[3] Borman VD, Belogorlov AA, Grekhov AM, Tronin VN. Multiplicity of metastable nonergodic states of a dispersed nonwetting liquid in a disordered nanoporous medium. *Eur Phys J B* 2014; 87:249.
[4] Zhao D, Huo Q, Feng J, et al. Nonionic Triblock and Star Diblock Copolymer and OligomericSurfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures. *J Am Chem Soc* 1998; 120: 6024-6036.
[5] Lisichkin GV, Fadeev AYu, Serdan AA, et al. *Chemistry of Graft Surface Compounds*. Moscow: Fizmatlit; 2003 [in Russian].
[6] Lowell S, Shields JE, Thomas MA, Thommes M. *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density*. New York: Springer; 2006.
[7] Borman VD, Belogorlov AA, Grekhov AM, et al. The percolation transition in filling a nanoporous body by a nonwetting liquid, *J Exp Theor Phys* 2005; 100:385.
[8] Park C-Y, Ihm S-K. New hypotheses for mercury porosimetry with percolation approach. *AIChE J* 1990; 36:1641-1648.